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Energy- and Electron-Transfer Quenching of Porphyrin Triplets by C_{60}[1]

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Energy- and electron-transfer from porphyrins in the triplet excited state to C_{60} in toluene and benzonitrile has been studied with Fourier transform EPR (FT-EPR). Pulsed-laser excitation of the systems magnesium tetraphenylporphyrin (MgTPP)/C_{60} and free-base octaethylporphyrin (OEP)/C_{60} in toluene gives rise to a resonance peak from C_{60} triplets ($^3C_{60}$) generated primarily by the energy-transfer process ^{3}MgTPP (^{3}OEP) + C_{60} → MgTPP (OEP) + $^3C_{60}$ as evident from the emissive spin polarization of the $^3C_{60}$ signal observed at early times. No FT-EPR signals from redox products could be detected. In benzonitrile, triplet energy transfer from ^{3}MgTPP or ^{3}OEP to C_{60} is a minor process. In this polar solvent photoexcitation of MgTPP/C_{60} produces FT-EPR spectra with signal contributions from MgTPP$^+$ and C_{60}^- in addition to the $^3C_{60}$ resonance. From the spin polarization and time profile of the signal from the anion radical, it can be deduced that the primary route of electron transfer is oxidative quenching of the porphyrin triplets, ^{3}MgTPP (^{3}OEP) + C_{60} → MgTPP$^+$ (OEP$^+$) + C_{60}^-. The reduction in $^3C_{60}$ lifetime indicates that C_{60}^- is generated as well by the reductive triplet quenching reaction $^3C_{60}$ + MgTPP (OEP) → C_{60}^- + MgTPP$^+$ (OEP$^+$).

Introduction

In recent years a number of studies concerned with the photophysics and photochemistry of porphyrin−fullerene systems have been reported. The investigations involved solutions of porphyrins and fullerenes (C_{60} and C_{70}),[2−4] solutions of C_{60} covalently linked to a porphyrin,[5] and an organized assembly of a porphyrin with C_{60} in a lipid bilayer.[6] Interest in these systems stems from possible applications in solar-energy conversion systems and optoelectronic devices.

Porphyrins and C_{60} have a number of properties that make them suitable as components in artificial reaction centers and molecular-scale electronic devices. The molecules absorb light in the visible region of the spectrum, intersystem crossing (isc) to the relatively long-lived triplet excited state occurs with close to 100% quantum yield,[7,8] and in the triplet state the porphyrins can be good electron donors,[9] whereas C_{60} is a good electron acceptor.[10,11]

A transient optical absorption study of zinc tetraphenylporphyrin (ZnTPP) with C_{60} or C_{70} in polar solvents by Nojiri et al.[2] shows that photoexcitation results in electron transfer from ZnTPP to the fullerene independent of which chromophore is excited. The following mechanisms were proposed to account for the photoinduced electron-transfer process:

$$C_{60} \xrightarrow{h\nu} {}^1C_{60} \xrightarrow{\text{isc}} {}^3C_{60}^* \xrightarrow{\text{P}} C_{60}^- + P^+ \tag{1}$$

$$P \xrightarrow{h\nu} {}^1P^* \xrightarrow{\text{isc}} {}^3P^* \xrightarrow{C_{60}} C_{60}^- + P^+ \tag{2}$$

Fujisawa et al.[3] demonstrated with the aid of time-resolved cw EPR (TREPR) that photoexcitation of porphyrins in the presence of C_{60} in liquid solution (toluene) can also lead to triplet energy transfer according to

$$P \xrightarrow{h\nu} {}^1P^* \xrightarrow{\text{isc}} {}^3P^* \xrightarrow{C_{60}} P + {}^3C_{60} \tag{3}$$

The authors also reported on a study of photoinduced electron and energy transfer from photoexcited porphyrins to C_{60} in benzonitrile carried out with pulsed EPR and TREPR.[4]

As the work by Fujisawa et al.[4] illustrates, for the study of porphyrin/C_{60} systems where excited-state quenching can involve competing paths, the application of Fourier transform EPR (FT-EPR) has advantages over transient optical absorption measurements. First, the magnetic resonance spectra show well-resolved peaks due to $^3C_{60}$ as well as electron-transfer product(s) that can be easily identified with the aid of information on *g* values and hyperfine splitting constants. This facilitates the study of the kinetics of electron- and energy-transfer processes. Second, spin polarization transfer accompanies the formation of $^3C_{60}$ by energy transfer. Since the resonance peak of C_{60} triplets carries the spin polarization signature of the precursor porphyrin triplet, this energy-transfer route of triplet C_{60} formation is readily identified. In the present study these features have been used to obtain information on the solvent dependence of electron- and energy-transfer quenching of porphyrin triplets by C_{60}.

Experimental Section

C_{60} (99.9%, SES Research), magnesium tetraphenylporphyrin (MgTPP, Aldrich), octaethylporphyrin (OEP, Aldrich), benzonitrile (99.9%, HPLC grade, Aldrich), and toluene (99.8%, HPLC grade, Aldrich) were used as received. In all solutions, the concentration of C_{60} (2×10^{-4} M) was kept constant and the porphyrin concentration was varied (2×10^{-4}, 4×10^{-4}, and 8×10^{-4} M). Under the experimental condition where the porphyrin concentration was 4×10^{-4} M, the ratio of laser light (532 nm) absorbed by porphyrin over that absorbed by C_{60} is 4 (4) and 9 (9.5) for MgTPP/C_{60} and OEP/C_{60} in toluene (benzonitrile), respectively. Porphyrin/C_{60} samples in toluene and benzonitrile were degassed on a high-vacuum line by several

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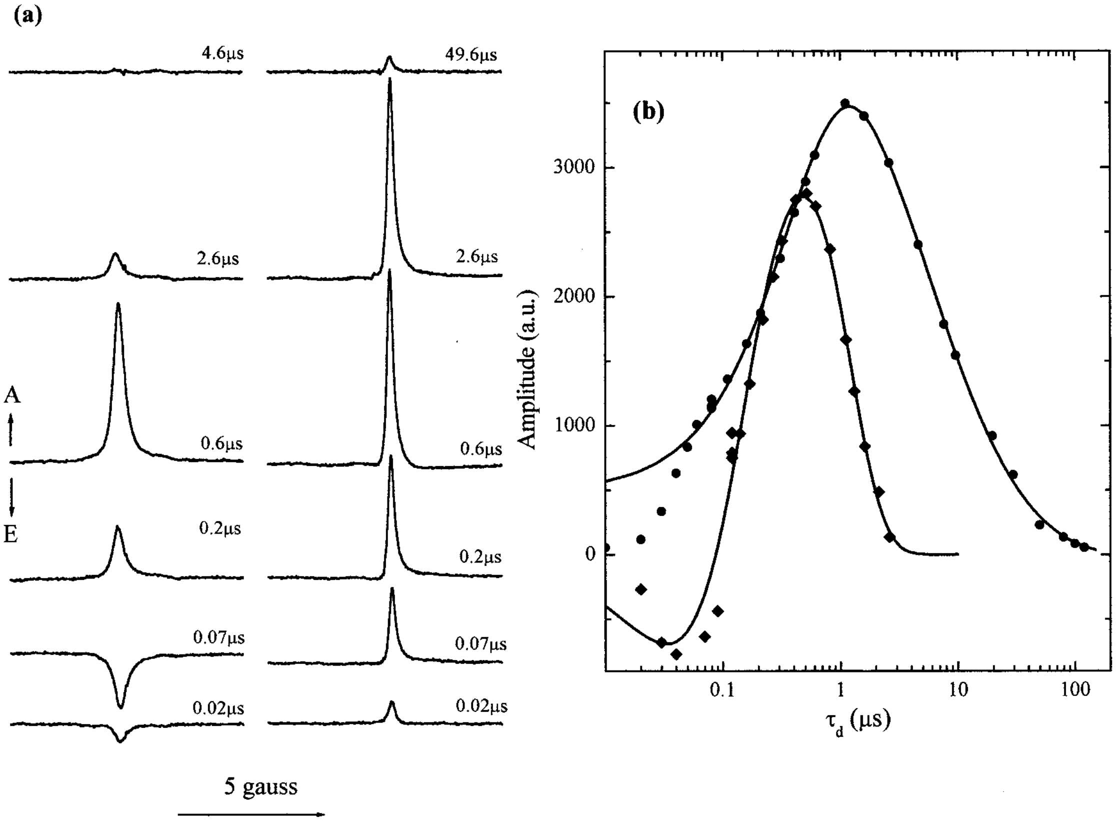

Figure 1. (a) FT-EPR spectra of $^3C_{60}$ produced by excitation of deaerated MgTPP (4×10^{-4} M)/C_{60} (2×10^{-4} M) (left) and C_{60} (2×10^{-4} M) (right) in toluene, for a series of delay times (τ_d) between laser and microwave pulses. (b) Time profiles of the $^3C_{60}$ signal intensity given by (◆) MgTPP/C_{60} and (●) C_{60} in toluene. Solid lines represent least-squares fits; see the text for the models used.

freeze−pump−thaw cycles and sealed off. Sample degradation over the time course of a series of measurements was negligible, establishing that the photoinduced processes studied are reversible.

FT-EPR measurements were performed with a home-built spectrometer.[12] The response of the sample to the $\pi/2$ microwave pulse was detected in quadrature with application of a CYCLOPS phase-cycling routine. Solutions held in the microwave cavity were excited with the second harmonic (532 nm) of a Quanta Ray GCR12 Nd:Yag laser (pulse width ∼8 ns, pulse energy ∼18 mJ, pulse repetition rate 10 Hz). In addition, FT-EPR measurements were carried out at different excitation wavelengths; the third harmonic of a Quanta Ray GCR12 Nd:Yag laser (∼18 mJ/pulse, 10 Hz) was used for excitation at 355 nm and a Lambda-Physik EMG103 MSC XeCl excimer laser for excitation at 308 nm (∼18 mJ/pulse, 10 Hz). All measurements were performed at room temperature. The FID produced by a $\pi/2$ (15 ns) microwave pulse was recorded for a series of delay times (10 ns < τ_d < 180 μs) between laser excitation and the microwave pulse. The FID was the time average of signals generated by a total of 4000 laser shots (1000 per phase) when porphyrins were present or 400 laser shots (100 per phase) for solutions containing C_{60} only. The amplitudes, phases, and line widths of resonance peaks were derived from the FIDs with a LPSVD analysis routine.[13]

Results and Discussion

MgTPP/C_{60} in Toluene. FT-EPR spectra obtained upon photoexcitation of a solution of MgTPP (4×10^{-4} M) and C_{60} (2×10^{-4} M) in toluene for a series of delay times between laser excitation and the microwave pulse are depicted in Figure 1a. For comparison, spectra given by a solution containing C_{60} (2×10^{-4} M) only are also displayed. The spectra show a single resonance peak at $g = 2.0012$ due to C_{60} in the photoexcited triplet state.[14−18]

The time profiles of the $^3C_{60}$ signal intensity are shown in Figure 1b. As noted previously,[15−18] triplets formed by direct excitation of C_{60} followed by isc from the singlet excited state are born with spin polarization (P_0) well below that at Boltzmann equilibrium (P_B). As a consequence, in the absence of porphyrin, the development of the absorption signal at early times (τ_d < 1 μs) is determined by P_0/P_B and the triplet spin−lattice relaxation rate (k_{T1C}). Signal decay is governed by a first-order process (k_d) and (second-order) triplet−triplet annihilation (k_{tt}).[19,20] A least-squares analysis of the data given by C_{60} (2×10^{-4} M) in toluene in the absence of porphyrin gave the following values for these parameters: $k_{T1C} = 2.2 \times 10^6$ s^{-1}, $k_d = 1.7 \times 10^4$ s^{-1}, $k_{tt}[^3C_{60}]_0 = 0.1 \times 10^6$ s^{-1}, and $P_0/P_B = 0.11$. These values are in satisfactory agreement with those reported previously.[15,18] Taking the value of k_{tt} (5.5×10^9 M^{-1} s^{-1}) reported in the literature for $^3C_{60}$ in toluene,[20] the triplet concentration at zero time $[^3C_{60}]_0$ is estimated to be 2×10^{-5} M.

A comparison of the spectra and time profiles presented in Figure 1 shows that the introduction of MgTPP has a significant effect on the time evolution of the $^3C_{60}$ signal. At short delay times (τ_d < 200 ns) the resonance is in emission rather than absorption. In addition, the triplet lifetime is strongly reduced. The effect of MgTPP on the development of the triplet signal is attributed to $^3C_{60}$ formation by energy transfer from ^{3}MgTPP (eq 3). At the C_{60} to MgTPP concentration ratio (1:2) used in this measurement, the porphyrin accounts for ∼80% of the absorption of light at 532 nm so that it is excited preferentially. Photoexcitation of MgTPP is followed by spin-selective isc, generating ^{3}MgTPP with excess population in the upper spin state of the triplet manifold.[21,22] The emissive ${}^3C_{60}$ signal observed at short delay times (<200 ns) provides unequivocal evidence that these triplets are produced by a triplet energy-transfer process from ^{3}MgTPP. A similar triplet–triplet energy-transfer process has been reported for the octaethylporphyrin/C_{60} system.[3]

When the porphyrin concentration is reduced to 2×10^{-4} M, the emissive signal is not observed. In this case, the signal contribution from triplets formed by direct excitation of C_{60} apparently exceeds that given by triplets formed by the energy-transfer route. The fact that at this porphyrin concentration the rate of signal growth matches the triplet spin–lattice relaxation rate found for ${}^3C_{60}$ in toluene (2.2×10^6 s^{-1}) is in agreement with this interpretation. Excitation at 355 nm, where the ratio of laser light absorbed by MgTPP (4×10^{-4} M) over that absorbed by C_{60} (2×10^{-4} M) is less than 0.6, also produces a ${}^3C_{60}$ signal that does not show an emissive contribution at early times. Furthermore, the signal intensity is a factor of 2 larger than that found upon excitation at 532 nm. In this case, the signal rise time matches the ${}^3C_{60}$ spin–lattice relaxation time as well, so that it can be concluded that triplets generated by direct excitation of the fullerene provide the major signal contribution.

The optical density at 532 nm of the C_{60} (2×10^{-4} M)/MgTPP (4×10^{-4} M) sample is about a factor of 4 higher than that of a solution containing C_{60} only. Hence, the overall triplet concentration produced by laser excitation is expected to increase by a factor of 4 as well. Even so, the maximum ${}^3C_{60}$ (absorptive) signal intensity, *corrected for the increased decay rate*, is only ~1.6 times larger than that given by C_{60} in toluene without the porphyrin. The fact that the transfer of triplet energy involves only a fraction of the porphyrin triplets formed is attributed to the near degeneracy of the energy levels[23] involved so that $[{}^3C_{60}]$ is governed by the equilibrium

$$ {}^3P + C_{60} \leftrightarrow P + {}^3C_{60} \tag{4} $$

In agreement with this interpretation, it is found that the concentration of C_{60} triplets formed upon excitation of MgTPP/C_{60} samples decreases as the MgTPP concentration is increased from 2×10^{-4} to 4×10^{-4} to 8×10^{-4} M. In a recent study Boyd et al.[24] found that fullerenes and porphyrins form complexes in toluene. This can also be a factor that plays a role in the attenuation of ${}^3C_{60}$ formation with increasing porphyrin concentration.

As noted above, the overall triplet concentration is estimated to be about 4 times as large as the ${}^3C_{60}$ concentration (~2×10^{-5} M) given by a solution containing no porphyrin. In the MgTPP (4×10^{-4} M)/C_{60} (2×10^{-4} M) solution, the concentration of C_{60} triplets formed is ~3×10^{-5} M. According to these estimates of the triplet concentrations, the equilibrium constant of eq 4 is near unity. The experimental results, therefore, point to nearly isoenergetic triplet levels. Given the uncertainty in triplet energy measurements, the literature values of 1.48 and 1.57 eV for ^{3}MgTPP[23,25] and ${}^3C_{60}$,[8,26] respectively, are consistent with this finding.

It is remarkable that the ${}^3C_{60}$ signal carries the signature of spin polarization transfer from ^{3}MgTPP. It signifies that triplet–triplet energy transfer is fast enough to compete with spin–lattice relaxation (T_{1P}) of the porphyrin triplets. Since k_{T1P} is expected to be on the order of 10^7 s^{-1}[27,22] and $[C_{60}] = 2 \times 10^{-4}$ M, the rate constant of energy (spin polarization) transfer must be in the 10^9 to 10^{10} M^{-1} s^{-1} range. This is a rather high rate for a triplet–triplet energy-transfer process with near-zero driving force.[28] In principle, spin exchange between spin-polarized ^{3}MgTTP and ${}^3C_{60}$ formed by direct excitation can provide an additional route of spin polarization transfer. However, at the triplet concentrations generated in these experiments, this process cannot play a significant role.

As shown in Figure 1b, the decay of the ${}^3C_{60}$ signal given by MgTPP/C_{60} in toluene is an order of magnitude faster than that observed for C_{60} alone. Measurements as a function of porphyrin concentration gave decay rates of 0.6×10^6, 1.1×10^6, and 2.2×10^6 s^{-1} for porphyrin concentrations of 2×10^{-4}, 4×10^{-4}, and 8×10^{-4} M, respectively, corresponding to a rate constant of 2.8×10^9 M^{-1} s^{-1}. Decay rates of 0.6×10^6 and 1.3×10^6 s^{-1} were found for porphyrin concentrations of 2×10^{-4} and 4×10^{-4} M, respectively, when the samples were excited with 355 nm light instead of 532 nm light. Thus, the triplet lifetime does not depend on whether ${}^3C_{60}$ is generated by energy transfer from ^{3}MgTPP or primarily by direct excitation of C_{60}. Furthermore, while increases in excitation light intensity (532 nm) cause increases in ${}^3C_{60}$ signal intensity, this also did not affect the kinetics so that the decay is independent of ^{3}MgTPP and ${}^3C_{60}$ concentrations as well.

A possible mechanism of triplet quenching is excited-state electron transfer. Because there is a dynamic equilibrium between ^{3}MgTPP and ${}^3C_{60}$ (eq 4), the triplet quenching reactions

$$ {}^3C_{60} + \mathrm{MgTPP} \rightarrow [C_{60}^{-}\cdots\mathrm{MgTPP}^{+}] \rightarrow C_{60} + \mathrm{MgTPP} \tag{5} $$

and

$$ C_{60} + {}^3\mathrm{MgTPP} \rightarrow [C_{60}^{-}\cdots\mathrm{MgTPP}^{+}] \rightarrow C_{60} + \mathrm{MgTPP} \tag{6} $$

will contribute to ${}^3C_{60}$ signal decay. As indicated in these reaction equations, these processes are not expected to yield redox products because in a nonpolar solvent such as toluene back electron transfer will occur before cage escape of radical ions takes place. $\Delta G°$ values for these electron-transfer reactions can be estimated using the Rehm–Weller equation[29]

$$ \Delta G° \approx E^{\mathrm{ox}}(\mathrm{D}) - E^{\mathrm{red}}(\mathrm{A}) - E_{\mathrm{T}} + \frac{e^2}{8\pi\epsilon_0 r_+}\left(\frac{1}{\epsilon} - \frac{1}{\epsilon'}\right) + \frac{e^2}{8\pi\epsilon_0 r_-}\left(\frac{1}{\epsilon} - \frac{1}{\epsilon''}\right) - \frac{e^2}{4\pi\epsilon_0 \epsilon R} \tag{7} $$

For electron-transfer quenching of ${}^3C_{60}$, with $E_{\mathrm{T}}({}^3C_{60}) = 1.57$ eV,[26] $E^{\mathrm{red}}(C_{60}) = -0.42$ V[10] (vs SCE, solvent benzonitrile), E^{ox}(MgTPP) = 0.54 V[30] (vs SCE, solvent butyronitrile), $2r_+ = 0.8$ nm, $2r_- = 0.71$ nm, $R = 0.75$ nm, ϵ(toluene) = 2.38, ϵ'(butyronitrile) = 24.83, and ϵ''(benzonitrile) = 25.9, eq 7 gives $\Delta G° \approx 0.04$ eV. Since $E_{\mathrm{T}}({}^3C_{60}) \approx E_{\mathrm{T}}({}^3\mathrm{MgTPP})$, the driving force for oxidative quenching of ^{3}MgTPP by C_{60} will have a similar value. Considering the fact that $\Delta G° \geq 0$, it appears unlikely that electron transfer can account for the short triplet lifetime. An alternative or competing triplet quenching path is suggested by the finding[24] that in toluene porphyrins show unusually strong interactions with fullerenes. This property apparently plays a role in the application of tetraphenylporphyrin-appended silicas for chromatographic separation of fullerenes.[31] It suggests the possibility of efficient deactivation of porphyrin and/or C_{60} triplets via an exciplex (${}^3[\mathrm{MgTPP}/C_{60}]$) formation step.

In principle, the values of all the rate constants governing ${}^3C_{60}$ formation and decay can be derived from a quantitative analysis of the time profile of the ${}^3C_{60}$ signal intensity.[4] However, because of the complexity of the systems studied here, such a comprehensive nonlinear least-squares analysis is unlikely

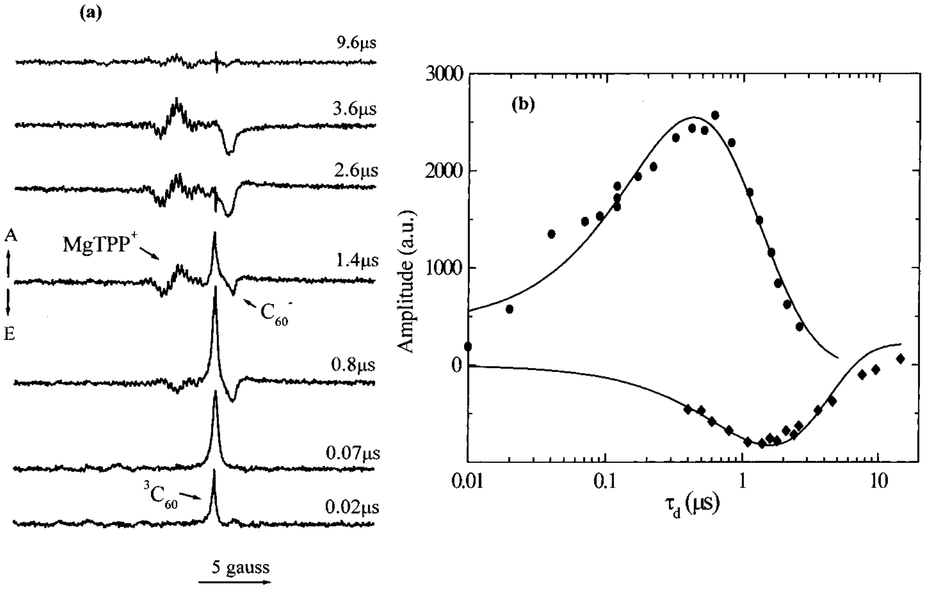

Figure 2. (a) FT-EPR spectra of free radicals produced by excitation of deaerated MgTPP (4×10^{-4} M)/C_{60} (2×10^{-4} M) in benzonitrile for a series of delay times (τ_D) between laser and microwave pulses. (b) Time profiles of (●) $^3C_{60}$ and (◆) C_{60}^- signal intensities given by MgTPP/C_{60} in benzonitrile. Solid lines represent least-squares fits based on models described in the text.

to provide a unique solution. For this reason, *semiquantitative* data on rates of ^{3}MgTPP spin−lattice relaxation, $^3C_{60}$ spin−lattice relaxation, and triplet energy transfer were derived from an analysis of the growing in of the $^3C_{60}$ signal. It takes into account (1) spin-polarized triplet porphyrin formation at $t = 0$, (2) ^{3}MgTPP spin−lattice relaxation (k_{T1P}), (3) exponential establishment of equilibrium concentrations of ^{3}MgTPP and $^3C_{60}$ (k_{en}), and (4)$^3C_{60}$ spin−lattice relaxation (k_{T1C}). A least-squares fit of the data obtained for MgTPP (4×10^{-4} M)/C_{60} (2×10^{-4} M)/toluene gave the following results: $k_{T1P} = 7.9 \times 10^6$ s^{-1}, $k_{T1C} = 3.4 \times 10^6$ s^{-1}, and $k_{en} = 1.4 \times 10^7$ s^{-1}. The value of k_{T1P} corresponds to a spin−lattice relaxation time T_1(^{3}MgTPP) of 125 ns. This is the order of magnitude predicted by theory[27] and is in line with the value of 230 ns derived for ^{3}MgTPP in ethanol at ∼−30 °C.[22]

MgTPP/C_{60} in Benzonitrile. Figure 2a shows the FT-EPR spectra generated by excitation of a solution containing C_{60} (2×10^{-4} M) with MgTPP (4×10^{-4} M) in benzonitrile for delay times ranging from 10 ns to 10 μs. A number of features distinguish the results obtained with this system from those given by MgTPP/C_{60} in toluene (Figure 1a). First, in addition to the $^3C_{60}$ resonance peak, an emissive multiline signal (hyperfine splitting, $a_H = 0.29$ G) develops at lower field over a period of about 1 μ. This is accompanied by the appearance of a broad emissive signal ($g = 2.0000$, $\Delta B_{pp} = 1.29(3)$ G) on the high-field side of the $^3C_{60}$ resonance. The multiline signal is assigned to the porphyrin radical cation, MgTPP$^+$, on the basis of the position and hyperfine splitting (literature values, $g = 2.0028$, $a_H = 0.28$ G, in dichloromethane).[32] The high-field line is assigned to the C_{60}^- anion since the g value matches the one reported for the electrochemically prepared species ($g = 1.9999$).[33] The line width of the resonance peak attributed to C_{60}^- (1.29 G) is considerably larger than the value of 0.103 G reported by Bennati et al.[17] for C_{60}^- in toluene, but closely matches the result reported by Stasko et al.[34] Second, in contrast to what is found for MgTPP/C_{60} in toluene at high porphyrin concentrations, the $^3C_{60}$ signal is in absorption independent of [MgTPP] and for all delay times. Finally, the $^3C_{60}$ signal is about a factor of 2 weaker than that found when toluene is used as solvent. Figure 2b displays the time profiles of the $^3C_{60}$ and C_{60}^- signal intensities; identical scales are used for the display of the signal intensities.

The results show that the triplet energy-transfer route of $^3C_{60}$ formation plays a minor role in benzonitrile. The absorptive $^3C_{60}$ signal can be attributed entirely to direct photoexcitation of C_{60}. The solid line in Figure 2b represents the least-squares fit based on a model in which $^3C_{60}$ signal growth is determined by spin−lattice relaxation and signal decay by a pseudo-first-order quenching reaction. In agreement with this interpretation, it is found that the rate of signal growth for all porphyrin concentrations (∼2.1×10^6 s^{-1}) matches the triplet spin−lattice relaxation rate found for $^3C_{60}$ in benzonitrile without porphyrin (2.0×10^6 s^{-1}).

As was found for MgTPP/C_{60} in toluene, $^3C_{60}$ signal decay is linearly dependent on porphyrin concentration. It increases from 0.4×10^6 to 0.9×10^6 to 2×10^6 s^{-1} for porphyrin concentrations of 2×10^{-4}, 4×10^{-4}, and 8×10^{-4} M, respectively, giving a value of 2.3×10^9 M^{-1} s^{-1} for the rate constant of $^3C_{60}$ quenching by MgTPP. By comparison, the decay rate found in toluene is 2.8×10^9 M^{-1} s^{-1}.

From the fact that the doublet radicals (MgTPP$^+$, C_{60}^-) at early times ($\tau_d < 1$ μs; cf. Figure 2a) give rise to overall emissive EPR signals, it can be concluded that the dominant signal contribution must be electron-transfer quenching of ^{3}MgTPP (eq 2). In this process, the (emissive) spin polarization of the porphyrin triplets is carried over to the doublet radicals (TM CIDEP).[35] Electron-transfer quenching of $^3C_{60}$ (eq 1) is expected to generate C_{60}^- as well,[2] but may make a minor signal contribution because of the low $^3C_{60}$ concentration and the absence of signal amplification by TM CIDEP. The signal due to reaction 1 is expected to be absorptive and apparently merely attenuates that given by the ^{3}MgTPP quenching process.

According to this interpretation, the time profile of the C_{60}^- signal intensity (cf. Figure 2b) depends on the rate of electron-transfer quenching of ^{3}MgTPP (k_{et}), spin−lattice relaxation rates of ^{3}MgTPP (k_{T1P}) and C_{60}^- (k_{T1D}), and the rate of back electron transfer. In the analysis of the C_{60}^- data it was assumed that signal growth primarily reflects electron transfer from spin-polarized ^{3}MgTPP and that signal decay is mainly due to relaxation of the C_{60}^- spin system to thermal equilibrium. The

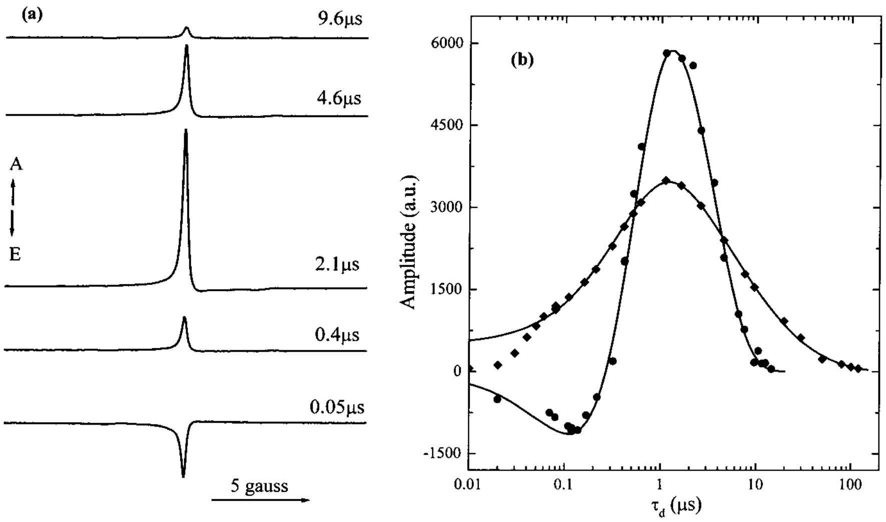

Figure 3. (a) FT-EPR spectra of $^3C_{60}$ produced by excitation of deaerated OEP (4×10^{-4} M)/C_{60} (2×10^{-4} M) in toluene for a series of delay times (τ_D) between laser and microwave pulses. (b) Time profiles of the $^3C_{60}$ signal intensity given by (●) OEP/C_{60} and (◆) C_{60} in toluene. Solid lines represent least-squares fits: see the text for the models used.

solid line in Figure 2b represents the result of the analysis. Rate constants are $k_{et} = 2.1 \times 10^9$ M^{-1} s^{-1} and $k_{T1D} = 0.5 \times 10^6$ s^{-1} ($T_{1D} = 2$ μs), respectively.

$^3C_{60}$ signal decay (2.3×10^9 M^{-1} s^{-1}) is attributed to excited-state electron transfer (eq 1), but as noted above, this triplet quenching process does not contribute significantly to the intensity of doublet radical signals. That the rate constant of $^3C_{60}$ signal decay closely matches that of C_{60}^- signal generation (2.1×10^9 M^{-1} s^{-1}) by electron-transfer quenching of ^{3}MgTPP (eq 2) is consistent with the fact that the triplet energies are virtually degenerate. It is of interest to note that the flash photolysis study of ZnTPP/C_{60} in benzonitrile by Nojiri et al.[2] gave quite distinct values for the rate constants of electron-transfer quenching of $^3C_{60}$ (1.1×10^9 M^{-1} s^{-1}) and ^{3}ZnTPP (0.48×10^9 M^{-1} s^{-1}). The large difference between these rate constants is remarkable in view of the fact that the literature value of the triplet energy of ZnTPP (1.59 eV[23]) is virtually identical to that of $^3C_{60}$.

The rate constants for electron-transfer quenching of ^{3}MgTPP and $^3C_{60}$ in benzonitrile are close to the diffusion-controlled limit, which is consistent[10] with the thermodynamic driving force of ~ -0.6 eV given by the Rehm–Weller equation.[29] Triplet C_{60} decay in toluene occurs at a rate (2.5×10^9 M^{-1} s^{-1}) very similar to the rate found in benzonitrile (2.3×10^9 M^{-1} s^{-1}). Since the driving force for electron transfer in toluene is $\sim$0.6 eV less than in benzonitrile, it is unlikely that this process can be the major route of triplet quenching. Instead, the result provides indirect support for the conclusion that, in a nonpolar solvent, triplet quenching via an excimer formation step route may play an important role.

OEP/C_{60} in Toluene and Benzonitrile. In many respects the results obtained with the OEP/C_{60} system mirror those obtained with MgTPP/C_{60}. As shown in Figure 3a, for OEP (4×10^{-4} M)/C_{60} (2×10^{-4} M) in toluene only the $^3C_{60}$ peak is observed. The signal is initially ($\tau_d < 200$ ns) in emission and subsequently turns into absorption, becoming stronger (cf. Figure 3b) than the signal given by C_{60} in the absence of OEP even though the triplet lifetime is considerably reduced by the addition of porphyrin. From this fact, it can be deduced that triplet energy transfer (eq 3) gives a major signal contribution. Similar time profiles are found as well at other OEP concentrations (8×10^{-4} and 2×10^{-4} M).

A comparison with the results obtained with MgTPP/C_{60} in toluene shows that, at similar concentrations, more $^3C_{60}$ is formed by energy transfer from ^{3}OEP than from ^{3}MgTPP. This reflects the fact that OEP absorbs more light than MgTPP at 532 nm and also may be due to the fact that the driving force for triplet–triplet energy transfer is somewhat higher (the triplet energy of OEP is given as 1.61 eV).[23] Even so, the maximum $^3C_{60}$ signal, corrected for variations in decay time, shows a gradual decrease as [OEP] is increased from 2×10^{-4} to 4×10^{-4} to 8×10^{-4} M, possibly reflecting a shift of the $^3\text{OEP} + C_{60} \leftrightarrow \text{OEP} + {}^3C_{60}$ equilibrium to the ^{3}OEP side.

The time evolution of $^3C_{60}$ signal growth was analyzed with the same model as the one used for MgTPP/C_{60}. Estimates of the rate constants of ^{3}OEP spin–lattice relaxation, $^3C_{60}$ spin–lattice relaxation, and triplet energy transfer derived from the analysis of the data given by C_{60} (2×10^{-4} M)/OEP (2×10^{-4} M) in toluene are 4.5×10^6, 2.5×10^6, and 1.0×10^7 s^{-1}, respectively. The ^{3}OEP spin–lattice relaxation time given by the data analysis, $\sim$220 ns, is in reasonable agreement with the value of 208 ns cited in the study of Fujisawa et al.[3]

Figure 3b shows that the $^3C_{60}$ lifetime is shortened substantially by the introduction of the porphyrin. It was found that the decay of the $^3C_{60}$ resonance peak is exponential with $k_d = 0.2 \times 10^6$, 0.4×10^6, and 0.7×10^6 s^{-1} for OEP concentrations of 2×10^{-4}, 4×10^{-4}, and 8×10^{-4} M, respectively, corresponding to a rate constant of 1.0×10^9 M^{-1} s^{-1}. As was found for MgTPP/C_{60} in toluene, this rate constant is not affected by changes in excitation light intensity or wavelength. With E^{ox}(OEP) = 0.81 V (vs SCE, solvent butyronitrile)[30] the Rehm–Weller equation gives $\Delta G° \approx 0.31$ eV for reductive quenching of $^3C_{60}$ by OEP in toluene (eq 1). Therefore, it is unlikely that the reduction in triplet lifetime is due to electron transfer. As in the case of MgTPP/C_{60} in toluene, there must be an alternative channel of triplet decay. A possible explanation is triplet quenching via an excimer formation step.[24]

Using benzonitrile as solvent, the FT-EPR spectra show resonance peaks due to $^3C_{60}$ and C_{60}^- (Figure 4a). In this system no resonance peaks due to the cation radical OEP$^+$ could be detected at any OEP concentration. The $^3C_{60}$ signal is in absorption for all delay times, whereas the anion radical signal is initially in emission. As was found in the case of the MgTPP/C_{60} system, in benzonitrile the formation of free radicals is

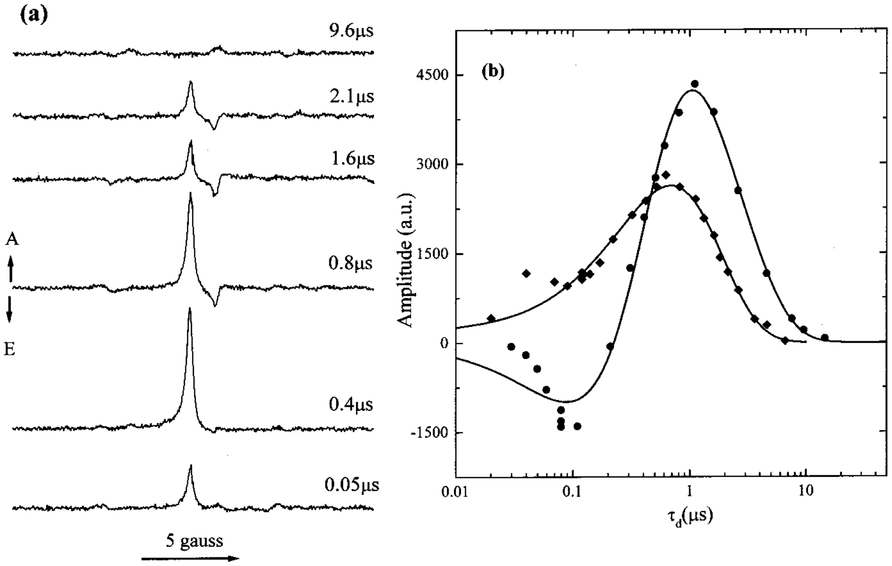

Figure 4. (a) FT-EPR spectra of free radicals produced by excitation of deaerated OEP (4×10^{-4} M)/C_{60} (2×10^{-4} M) in benzonitrile for a series of delay times (τ_D) between laser and microwave pulses. (b) Time profiles of the $^3C_{60}$ signal intensity given by (●) OEP/C_{60} in toluene and (◆) C_{60} (2×10^{-4} M)/OEP (4×10^{-4} M) in benzonitrile. Solid lines represent least-squares fits; see the text for the models used.

promoted and the oxidative quenching of ^{3}OEP by C_{60} (eq 2) is the major route of porphyrin triplet decay. Evidence for this is the fact that the relatively weak $^3C_{60}$ signal is in absorption at all times and apparently stems from direct excitation of C_{60}. It also accounts for the observation of the emissive C_{60}^- resonance peak (cf. Figure 4a).

Assuming that $^3C_{60}$ signal decay is governed by electron-transfer quenching by OEP (eq 1), a least-squares analysis of the data given by C_{60} (2×10^{-4} M)/OEP (4×10^{-4} M) gives a value of 2.1×10^9 M^{-1} s^{-1} for the electron-transfer rate constant.

Concluding Remarks

The FT-EPR study establishes that encounters of porphyrin triplets with C_{60} can lead to triplet energy transfer (eq 3) or electron transfer (eq 2). The competition between these two processes shows a strong solvent dependence. For the porphyrins MgTPP and OEP in nonpolar solvents, the energy-transfer path makes a significant contribution to porphyrin triplet quenching as evident from the characteristic spin polarization signature it imposes on the $^3C_{60}$ resonance. In the case of OEP (4×10^{-4} M)/C_{60} in toluene, the $^3C_{60}$ signal intensity, *corrected for the increased decay rate,* is a factor of 2 stronger than that given by direct excitation of C_{60} in the absence of porphyrin. Even for MgTPP (4×10^{-4} M)/C_{60} in toluene, where the triplet energies are virtually isoenergetic, the $^3C_{60}$ signal corrected for the fast decay rate is 1.5 times larger than that found when C_{60} is directly excited. From the relative magnitudes of the $^3C_{60}$ signal generated by triplet energy transfer, it can be deduced that (in toluene) $E_T(C_{60}) \approx E_T(\mathrm{MgTPP}) < E_T(\mathrm{OEP})$.

A change in solvent from *nonpolar* (toluene) to *polar* (benzonitrile) results in a strong reduction of the $^3C_{60}$ yield. This effect is attributed to an increase in the relative importance of the electron-transfer quenching path (eq 2). Similar solvent effects have been found in studies of quenching of triplet 1-nitronaphthalene by carotenoids,[36] sodium nitrite, and *trans*-stilbene,[37] and aromatic ketone triplets by organic dyes.[38] In the case of the nitronaphthalene/carotenoid systems, triplet quenching by electron transfer is strongly exergonic in both polar and nonpolar solvents. Even so, only triplet energy transfer is observed when cyclohexane is used as solvent, whereas in methanol the electron-transfer quenching reaction makes a strong contribution.[36]

In the porphyrin/C_{60} systems the change in solvent is not expected to affect the energy difference between the triplets significantly. By contrast, the $\Delta G°$ values of the triplet porphyrin electron-transfer quenching reactions estimated with the Rehm–Weller equation[29] show a pronounced change upon going from toluene to benzonitrile. For MgTPP (OEP)/C_{60}, the thermodynamic driving force for the porphyrin electron-transfer quenching drops from 0.04 (0.31) eV in toluene to -0.69 (-0.42) eV in benzonitrile. This suggests that the solvent-induced shift in relative importance of the two ^{3}P quenching processes is due to a change in thermodynamic driving force of the electron-transfer reaction. Support for this interpretation is provided by the flash photolysis study of triplet C_{60} quenching by tritolylamine by Biczòk et al.[11] These authors found rate constants of 8.5×10^7 and 3.5×10^9 M^{-1} s^{-1} in toluene and benzonitrile, respectively.

A remarkable feature is that the $^3C_{60}$ lifetime in the presence of the porphyrins is strongly reduced even in toluene where electron-transfer quenching is not expected to play a role. In an NMR study of fullerene/porphyrin systems in toluene, Boyd et al.[24] found evidence of complex formation apparently driven by strong π–π interactions between the molecules. This could provide for a near-diffusion-controlled triplet quenching mechanism.

In some earlier EPR studies of reductive quenching of $^3C_{60}$, no signal from the anion radical was detected.[4,15] In the present study a resonance peak due to the C_{60}^- anion generated by electron transfer from ^{3}MgTPP and ^{3}OEP to C_{60} in benzonitrile has been identified. While there is general agreement with regard to the *g* value of the EPR signal from C_{60}^- (2.000),[17,33,34] reported values of the line width of the resonance peak vary widely. The line width of the signal (~1 G) found in the present study is the same, within experimental error, as that listed for the signal attributed to the anion radical in the study of Stasko et al.[34] However, in an FT-EPR study of reductive quenching of $^3C_{60}$ in toluene, Bennati et al.[17] gave a value that is about an order of magnitude smaller. On the other hand, cw EPR measurements on electrochemically generated C_{60}^- carried out by Schell-Sorokin et al.[39] gave much broader signals than those reported here.

The reason for the remarkable variation in results obtained in EPR studies of the anion radical of C_{60} is not understood at this time. It may be related to the orbital degeneracy of the electronic state of C_{60}^- and the formation of aggregates at higher concentrations. It is known that organic free radicals with orbitally degenerate ground states can have unusually short spin−lattice relaxation times as a result of the dynamic Jahn−Teller effect.[40] Because of the degeneracy of the electronic state of C_{60}^-, the T_1 of the radical may be strongly affected by perturbations introduced by aggregate formation.

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